

Adsorption of nickel (II), cadmium (II) and lead (II) from aqueous solution using chitosan / raphia palm composite

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Abstract. Adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} from aqueous solution by chitosan / raphia palm activated carbon composite (CRPAC) material prepared in the form of beads have been investigated through batch mode adsorption process. The results obtained indicated that the modification of the chitosan by coating with raphia palm tends to increase the capacity of the chitosan as an adsorbent. The adsorption of the studied metals onto CRPAC was found to be favoured by Freundlich isotherms and was influenced by pH, contact time, concentration, biomass and dose. The kinetic studies showed that the adsorption followed a pseudo-second-order model with chemisorption mechanism being favoured. Thermodynamic study on the adsorption capacity of the adsorbents indicated that the adsorption is spontaneous (ΔG_{ads}^0 were negative), endothermic (ΔH_{ads}^0 values were positive) and occurred with increasing degree of orderliness rather than disorderliness.

Keywords: Adsorption, chitosan, raphia palm, polymer, water pollution.

1 Introduction

Heavy metal pollution has become a serious threat today and a matter of great environmental concern as heavy metals are non-degradable and thus persistent in the environment [1]. Technologies available for the removal of heavy metals from aqueous solutions include: adsorption, ion-exchange membrane, electro-chemical treatment, reverse osmosis, separation, oxidation and reduction, chemical precipitation, filtration, evaporation and electrolysis [2]. Adsorption has been found to be one of the best options available for the removal of heavy metals from aqueous solution [1, 3]. The process have been found to be highly efficient for the removal of metals in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances.

Recent studies have shown that heavy metals can be removed by using plant materials such as palm oil fruit bunch[4], soar sop seeds[5], chitosan [6 – 8], modified cassava fibre [9], Bombamalabaricum fruit shell [10], coconut shell [11], coconut husk peatmoss [12], bio waste materials like saw dust, peapod, cotton and mustard seed cakes [13]. Among the many other low cost absorbents, chitosan has been reported to have the highest sorption capacity for several metal ions and dyes [8]. However chitosan used as adsorbent has drawn attentions due to the following reasons:

- It has high contents of amino and hydroxyl functional groups.

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- It is slightly soluble at low pHs – This poses problems for developing commercial applications of it.
- It is soft and has a tendency to agglomerate or form a gel in aqueous solutions.
- Its active binding sites are not readily available for sorption. It has been reported that transport of the metal contaminants or dye ions to the binding sites of adsorbent plays a very important role in process design.

There is need to provide physical support and increase the accessibility of the metal binding sites for process applications of chitosan hence this research. Attempt was made in the current research to produce an adsorbent that is capable of overcoming the shortcomings highlighted above by coating chitosan on the surface of raphia palm fruit. *Raphiahookeri* also known as “Raphia palm tree” in English belongs to of the family of Palmaea. It is found in the lowland region of Nigeria, many tropical countries and some parts of India. Studies have shown that it is feasible to prepare chars with sufficient densities and high porosity from raphia palm fruit waste [14].

The present study is aimed at using chitosan / raphia palm composite (CRPC) for the adsorption of nickel (II), cadmium (II) and lead (II) from aqueous solution. The combination of the useful properties of the activated carbon prepared from the Raphia palm fruit and that of natural chitosan, could introduce a composite matrix with many application and better adsorption properties.

2 Material and Methods

2.1. Sample Collection

All reagents used for the study were of analar grade. The Raphia palm fruit used were collected from Ikot Ekpene Akwalbom State Nigeria. The endocarp (nut) which was separated from the mesocarp and epicarp were washed and dried in an oven at 60°C for 24 hours. The dried substance was grounded thoroughly by ball mill abrasion and sieved into 180 µm particle size.

The chitosan used in the study is as supplied by Sigma Aldrich Chemicals. It was washed three times with deionized water and dried in an oven at 50 °C before use.

2.2. Preparation of Raphia Palm Activated Carbon

100.00 g of the sieved material were mixed with 500.00 ml of 1 M phosphoric acid (purity 85 %) in a plastic container. The mixture was transferred into copper crucibles and heated in an oven at 120 °C for 30 minutes with occasional stirring before it was removed and left overnight. After cooling, the activated sample was repeatedly washed with ionised water until the pH of the filtrate fall between 6.0 - 6.5. The sample was then dried in an oven at 105 °C and stored in desiccators for adsorption experiment.

2.3. Preparation of chitosan / raphia palm composite beads

The method used in the preparation of the chitosan / raphia palm composite (CRPAC) is as described by Hasan *et al.* [15]. 1 g chitosan was dissolved in 1 mol /L acetic acid (100 mL) and mixed with 1 g of the activated raphia palm ash prepared earlier in section 2.2 above and agitated for 60 minutes. The resultant viscous solution was sprayed dropwise through a syringe, at a constant rate, into neutralization solution containing 15 % Sodium hydroxide and 95 % ethanol in a volume ratio of 4:1. They were left in the solution for 1 day [8]. The formed composite beads were washed with deionized water until solution become neutral and then stored in distilled water.

2.4. Adsorption experiment

The effects of mass of adsorbent dose, pH, contact time, initial metal ions concentration and temperature in order to ascertain the optimum conditions, kinetics, as well as thermodynamic nature of the adsorption

process of Pb (II), Cd (II), and Ni (II) on the chitosan / raphia palm activated carbon was studied by performing different equilibrium sorption tests as reported by Benkli *et al*[16]. In each case, the concentration of the metal ion adsorbed was determined using Atomic Absorption Spectrometer, AAS (Analyst 100 PerkinElmer). The amount of metal adsorbed at equilibrium, q_e (mg/g), and the percentage of metal ion adsorbed (% Rem) were determined using the following equation:

$$\% \text{Rem} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{MV(C_0 - C_e)}{1000}$$

where q_e is the amount of adsorbate ion adsorbed in milligram per gram of the adsorbent, C_0 is the initial concentration of the metal ion before adsorption process, C_e is the equilibrium concentration of the metal ion in the filtrate after adsorption process and M is the mass in gram of the adsorbent, V is the volume of the solution in ml.

3. Results and Discussions

3.1. Effect of pH

Variation of pH on the adsorption of Pb (II), Cd(II), and Ni(II) by the adsorbents chitosan / raphia palm composite (CRPAC) and chitosan activated carbon (CAC) is presented in Figures 1. From this result, it can be seen that the adsorption of the metal ions increased with increase in pH of solution to a maximum value of 6.5 and thereafter decreases. It is commonly agreed that the adsorption of metal ions increases with increasing pH as the metal ionic species become less stable in solution [17]. According to Ameh and Odoh [3], decrease in the amount of metal ions removed by the adsorbents above pH 6 may be due to occupation of the adsorption sites by anionic species which retards the approach of such ions further toward the sorbent surface. As the pH is increased towards the alkaline, the overall surface charge on the adsorbent became negative and adsorption decreases. Within the pH range of 3.5 - 6.5, both CAC and CCRPAC adsorbed the metal ions in the order of Ni (II) > Pb (II) > Cd (II) respectively.

It is observed from the result presented that CCRPAC adsorbed more of the metal ions than CAC at the same pH. This is due to the fact that modification of chitosan by coating with raphia palm activated carbon as in the case of CRPAC altered surface characteristic of the adsorbent leading to increase ion uptake [18].

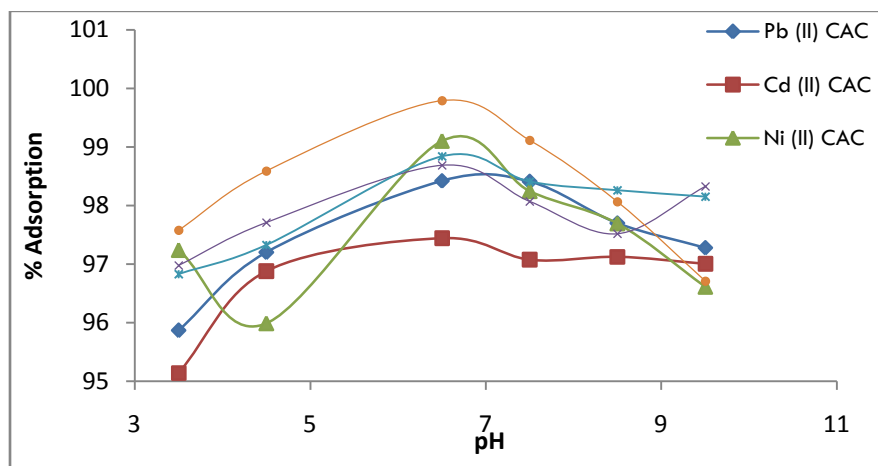


Fig 1. Effect of pH on removal of the studied metal ions using CAC and CRPAC

3.2 Effect of mass of adsorbent

Adsorption capacities of CRPAC and CAC for Cd^{2+} , Ni^{2+} and Pb^{2+} were also found to be influenced by mass of the respective adsorbents. Table 1 shows concentrations of studied metals adsorbed by various grams of the respective adsorbents at 303 K. From the results obtained, it can be seen that the quantity of the metal ions removed by CRPAC and CAC increases with increased in the adsorbent dosage at first but tend to decrease after a critical mass of 3g. The increase with increase in dosage is attributed to the availability of more adsorptive sites or increase in surface area at high concentration of the adsorbent sites [19]. The decrease in the quantity of the metal ions after a maximum of 3g may be due to desorption after the adsorption of the heavy metal has reached its maximum value. This result also suggests that after a certain dosage of adsorbent with the maximum adsorption attained, the amount of metal ion bound them and the amount of free ions in solution remain constant even with further addition of the adsorbent. The trend for the adsorption of the metal ions with dosage followed the order $\text{Pb(II)} > \text{Ni(II)} > \text{Cd(II)}$ respectively. This difference might be due to the difference in the chemistry of the three metal ions which may include ionic size, electronegativity, etc. Also, CRPAC performed better than CAC in the adsorption of the metals from solution as expected.

Table 1: Amount of heavy metal adsorbed by various sizes of CAC and CRPAC from aqueous solution at 303 K

Dosage(g)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)
0.25	88.590 $\pm$ 0.392	88.900 $\pm$ 0.042	90.999 $\pm$ 0.146	94.799 $\pm$ 0.282	95.897 $\pm$ 0.251	96.999 $\pm$ 2.027
0.50	89.999 $\pm$ 0.829	90.000 $\pm$ 0.084	93.918 $\pm$ 0.146	95.028 $\pm$ 0.033	96.772 $\pm$ 0.200	97.288 $\pm$ 0.713
1.00	92.091 $\pm$ 0.829	92.970 $\pm$ 0.084	94.353 $\pm$ 0.032	96.346 $\pm$ 0.311	97.368 $\pm$ 0.373	98.100 $\pm$ 1.178
2.00	93.999 $\pm$ 0.829	94.784 $\pm$ 0.011	95.416 $\pm$ 0.080	97.626 $\pm$ 0.211	98.678 $\pm$ 0.162	98.971 $\pm$ 1.020
3.00	94.260 $\pm$ 0.690	95.744 $\pm$ 0.034	96.775 $\pm$ 0.098	98.454 $\pm$ 0.141	99.700 $\pm$ 0.171	99.920 $\pm$ 0.109
8.00	92.570 $\pm$ 0.245	93.112 $\pm$ 0.234	95.400 $\pm$ 0.098	96.400 $\pm$ 0.289	97.276 $\pm$ 0.411	98.110 $\pm$ 1.088

3.3. Effect of temperature

The effect of the solution temperature on the adsorption capacity of the studied adsorbents were investigated for Pb (II), Ni (II) and Cd (II) ions solutions at initial metal ions concentration of 100 mg/l and adsorbent dosage of 3 g. The amount of heavy metal adsorbed was plotted against temperature and are presented in Figure 2.

The plot revealed that the percentage removal of Cd (II) by CAC increased from 92.53% to 93.00 % with an increase in temperature from 303 to 343 K. Similarly, the CAC adsorbed 93.95 mg/g of Pb (II) at the temperature 303 K which increased to 95.11mg/g at the temperature 343 K. The adsorption of Ni (II) ion on the same adsorbent showed that 90.98mg/g was adsorbed at the temperature of 303 K which increased to 92.84 mg/g at temperature 343 K. The adsorption of the metal ions by the modified adsorbents showed that CRPAC adsorbed 99.29 mg/g at 303 K, 99.44 mg/g at 343 K, of Cd (II) ions 97.52 mg/g at 303 K, 98.68 mg/g at 343 K of Ni (II), while 99.27 mg/g at 303 K, and 99.49 mg/g at 343 K of Pb (II) ion was adsorbed. From these results, it is observed that for both the CAC and CRPAC adsorbents, the amount of the three metal ions adsorbed increased with increase in temperature. This indicates that the adsorption process is endothermic. This might be attributed to the increase surface activity between the metal ions and the unmodified and modified adsorbent which is endothermic in nature. Similar results of increase adsorption with increase in temperature have been reported by Ameen *et al.*, [20] and Oladunni et al [2].

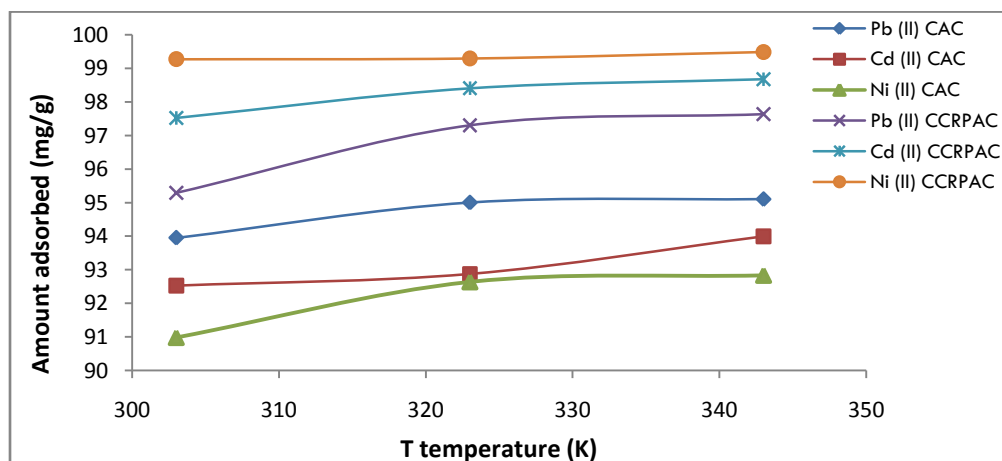


Fig 2. Plot of Amount of Studied metal ions adsorbed onto CAC and CRPAC against Temperature

3.4. Effect of contact time

Figure 3 shows the variation of the concentrations of Cd^{2+} , Ni^{2+} and Pb^{2+} adsorbed by CAC and CRPAC from aqueous solutions at various time intervals. From the results, it is indicative that the amount of metal ions adsorbed increased with increase in time for the two adsorbents. The increase of the metal ion removal with increase in contact time can be explained by the affinity of the adsorbents towards metal ions [21]. There was also significant increase in the amount adsorbed by CRPAC and CAC for all the three studied metal ions.

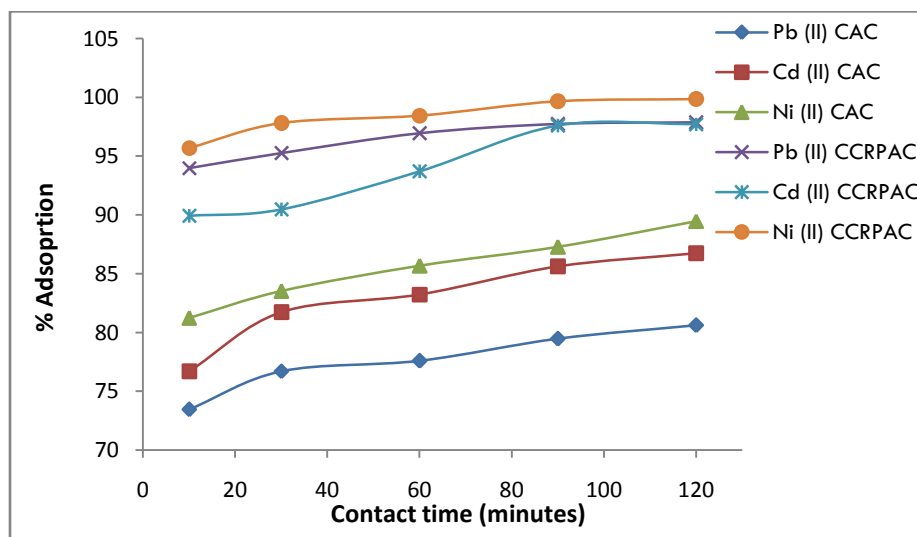


Fig 3. Variation of the concentrations of Cd^{2+} , Ni^{2+} and Pb^{2+} adsorbed by CAC and CRPAC from aqueous solutions at various time intervals

3.5 Effect of initial metal ions concentration

The amount of Cd^{2+} , Ni^{2+} and Pb^{2+} adsorbed by CAC and CRPAC from aqueous solutions containing various concentrations of the metals at 303 K are presented in Table 2. From the results presented, it can be seen that the adsorption capacity of the studied adsorbents for Cd^{2+} , Ni^{2+} and Pb^{2+} increases with increase in the concentration of the metal ions in solution. This increase could be due to the availability of

the uncovered surface areas of the adsorbents since the adsorption kinetics depends on the surface area of the adsorbent [22]. These could also be explained in terms of the progressive increase in the electrostatic interaction between the metal ion and the adsorbent active site; moreover, more adsorption sites were being covered as the metal ions concentration increased [23]. Besides, higher initial concentration led to an increase in the affinity of the metal ion towards the active sites [24].

It was also found that the maximum concentrations of Cd^{2+} , Ni^{2+} and Pb^{2+} adsorbed by CRPAC was found to be were slightly higher than those adsorbed by CAC (i.e. Cd^{2+} : 99.93 and 90.73 mg/g; Ni^{2+} : 99.92 and 90.04 mg/g; Pb^{2+} : 99.84 and 90.49 mg/g for CRPAC and CAC respectively). This indicates that modification of the chitosan by coating with raphia palm tends to increase the capacity of the chitosan as an adsorbent.

Table 2. Amount of heavy metal adsorbed by CAC and CRPAC from aqueous solution containing various concentrations of the metals at 303 K

C (mg/l)	CCRPAC			CAC		
	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)
10	12.723±0.015	11.388±0.015	15.978±0.138	10.153±0.113	10.110±0.023	12.013±0.431
20	22.174±1.425	20.284±0.811	25.117±0.523	18.257±0.422	19.746±0.992	18.818±0.777
40	45.170±0.418	40.923±0.152	47.984±0.194	40.612±0.999	40.004±0.120	41.223±0.015
60	62.677±0.185	60.945±0.216	63.254±0.138	61.001±0.026	60.166±0.252	61.270±0.718
80	82.173±1.915	80.945±0.158	82.908±0.604	80.201±0.314	80.315±0.432	79.243±0.152
100	99.934±0.415	99.921±0.015	99.842±0.204	90.734±0.300	90.042±0.009	90.488±0.135

3.6 Adsorption kinetics modeling

The kinetics of the adsorption of the studied metal ions on CAC and CRPAC was tested with respect to first-order model of Lagergren and pseudo-second-order kinetic model [25].

The linear forms of pseudo first - order kinetics is given by Equations (3)

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (3)$$

Where q_e and q_t are the amount of heavy metal ions adsorbed at equilibrium and at time, t (respectively mg/g) and k_1 is the first order rate constant (min^{-1}). From equation 3, a plot of $\ln(q_e - q_t)$ versus t should be liner if a pseudo first order kinetic is obeyed. However, when adsorption data obtained for the studied adsorbents were fitted into the model expressed by equation 3, values of R^2 obtained from the plots (plots not shown) were very low indicating that the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by CAC and CRPAC is not consistent with a pseudo first order kinetics.

The pseudo second order adsorption rate equation can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The implication of equation 4 is that a plot of t/q_t versus t should be linear if this model is adhered to. Figure 4 shows a pseudo second order kinetic plots for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by CAC and CRPAC. Kinetic parameters obtained from slopes and intercepts of the plots are presented in Table 3. From the results obtained, it can be seen that higher values of rate constant (k_2) were obtained. Also, the correlation coefficient (R^2) values obtained were close or equal to 1. The high values of pseudo-second order rate constant and the high correlation coefficient indicates that the pseudo-second order provides the best description of the experimental data obtained for the adsorption of the studied metal ions onto CAC and CRPAC.

It was also observed that the k_2 values which give an idea of the surface porosity for the adsorption of Ni^{2+} and Pb^{2+} by CRPAC adsorbents were higher than those obtained from the CAC adsorbents. This may

be due to the modification of CAC. According to Orike [26], the higher the k_2 value, the more porous is the adsorbent surface.

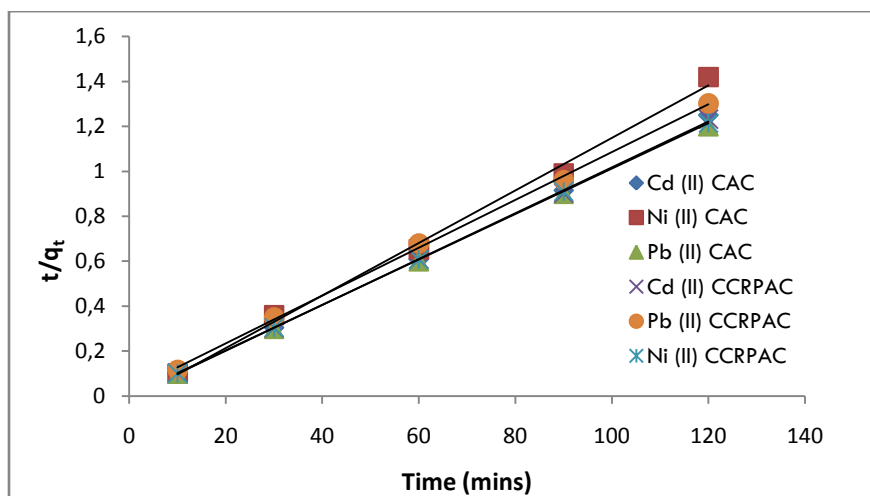


Fig 4. Variation of t/q_t with t (pseudo second order kinetic) for the for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by CAC and CRPAC

Table 3. Pseudo second order adsorption parameters for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by CAC and CRPAC

Adsorbent	Metal ion	slope	q_e	k_2	R^2
CAC	Cd^{2+}	0.0101	-0.006	-1.71E-02	0.9985
	Ni^{2+}	0.0100	0.0062	1.62E-02	0.9988
	Pb^{2+}	0.0101	0.0006	1.64E-01	1.0000
CRPAC	Cd^{2+}	0.0100	0.0008	1.23E-01	1.0000
	Ni^{2+}	0.0102	0.0001	1.00E+00	1.0000
	Pb^{2+}	0.0099	0.0331	2.96E+01	0.9994

The kinetic results were further analyzed using the intraparticle diffusion model proposed by Weber Moris [27] to elucidate the diffusion mechanism given by equation 5:

$$q_t = k_p t^{1/2} \quad (5)$$

Where k_p is the intraparticle diffusion rate constant. According to this model, the intra particle diffusion will be the sole rate-limiting process if the plot of q_t vs. $t^{1/2}$ is linear and passes through the origin [28-29].

The plot of q_t versus $t^{1/2}$ for the adsorption of metal ions by CAC and CRPAC is shown in Figures 5. It can be seen that the plots presented gave straight lines. However, none of the plots passed through the origin. Values of the intra particle diffusion constant (k_p) were obtained from the slopes of the linear portions of the plots and are presented in Table 4. The low correlation coefficient (R^2) obtained (Table 4) with plot lines that does not passes through the origin (Figure 5) indicates that although intra particle diffusion was involved in the adsorption process, it was not the rate-controlling step [30]. The results obtained in this study are comparable to that reported for the activated carbon prepared from some plant sources [31-32].

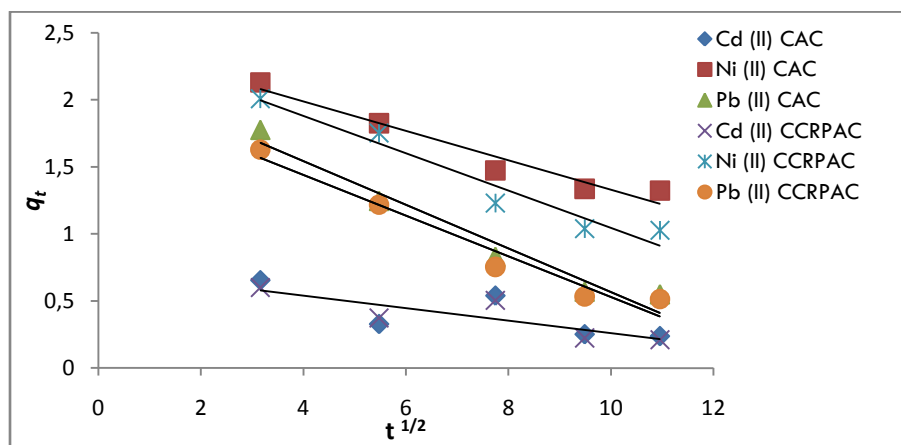


Fig 5. Intraparticle diffusion plot for the adsorption of Cd(II), Pb(II) and Ni(II) ions onto CAC and CRPAC

Table 4. Intraparticle Diffusion Model Constant

Metal ions	CAC		CRPAC	
	K_p	R^2	K_p	R^2
Cd^{2+}	-0.045	0.591	-0.046	0.718
Pb^{2+}	-0.109	0.948	-0.139	0.946
Ni^{2+}	-0.162	0.954	-0.151	0.957

3.7. Adsorption Isotherms

To further facilitate the estimation of the adsorption capacities of the various metal ions concentrations, data obtained from the equilibrium studies were used to fit curves for different adsorption models (Langmuir, Freundlich, Flory-Huggins and Dubinin-Raduskerich) and it was found that the adsorption of the studied metal ions by both CRPAC and CAC can best be described by Freundlich adsorption isotherm which linearized form can be represented as equation 6 [32];

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), K_F is the Freundlich adsorption constant (mg/g) (dm^3/g), n is related to the adsorption capacity and C_e is the equilibrium concentration of the adsorbate (mg/L). From equation 6, the Freundlich isotherm plot is fitted by plotting values of $\log q_e$ against $\log C_e$ with the slope and intercept of the plot equal to the reciprocal of n and K_F respectively. Figures 6 and 7 shows the Freundlich adsorption isotherms for the adsorption of Ni^{2+} , Cd^{2+} and Pb^{2+} by CCRPAC and CAC respectively. Values of Freundlich adsorption parameters deduced from the plots are presented in Table 5. From the results obtained, it can be seen that values of R^2 approached unity in all cases indicating the application of Freundlich adsorption model for the adsorption of Pb^{2+} , Cd^{2+} and Ni^{2+} onto CRPAC and CAC. The suitability of the Freundlich isotherm to the adsorption of the studied ions implies that there is multilayer adsorption with non-uniform distribution over the heterogeneous surface [33]. The value of $1/n$, according to Gimba et al [34], is an index for measuring the adsorption intensity. Generally, when the value of $1/n$ is in the range, 0 to 1, is a measure of the adsorption intensity or surface heterogeneity. The surface becomes more heterogeneous as the value of n tends toward 0 [34]. On the other hand, $1/n$ value less than unity suggest chemisorption mechanism whereas $1/n$ value above unity point toward cooperative adsorption. Therefore, the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} supports the mechanism of chemical adsorption since values of $1/n$ obtained in this research are below unity.

It has been found that the Freundlich adsorption constant (K_F) is related to the free energy of adsorption according to the following equation [35].

$$\Delta G_{ads}^0 = -2.303RT \log K_F \quad (7)$$

where R is the universal gas constant and T is the temperature. Values of ΔG_{ads}^0 calculated from equation 7 as presented in Table 5 indicated that the adsorption process is spontaneous and feasible.

Table 5: Freundlich parameters for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by CAC and CRPAC

Adsorbent	Metal ions	Slope	Intercept	1/n	ΔG^0 (J/mol)	R^2
CAC	Cd^{2+}	1.06245	-0.1148	0.94	-689.02	0.9872
	Ni^{2+}	1.1722	-0.3250	0.85	-172.11	0.9887
	Pb^{2+}	1.0011	0.0058	0.93	-233.65	0.9999
CRPAC	Cd^{2+}	1.0356	-0.0506	0.96	-293.56	0.9987
	Ni^{2+}	1.0408	-0.0322	0.95	-192.23	0.9964
	Pb^{2+}	1.0155	-0.0344	0.97	-196.64	0.9925

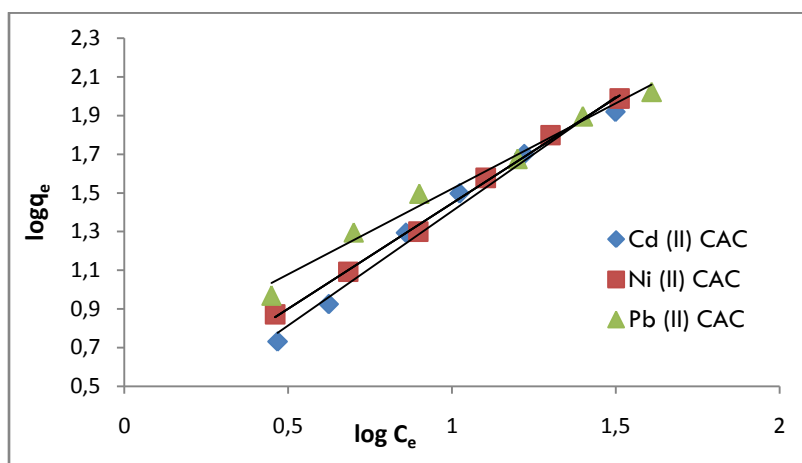


Fig 6. Freundlich isotherm model plots for adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} onto CAC

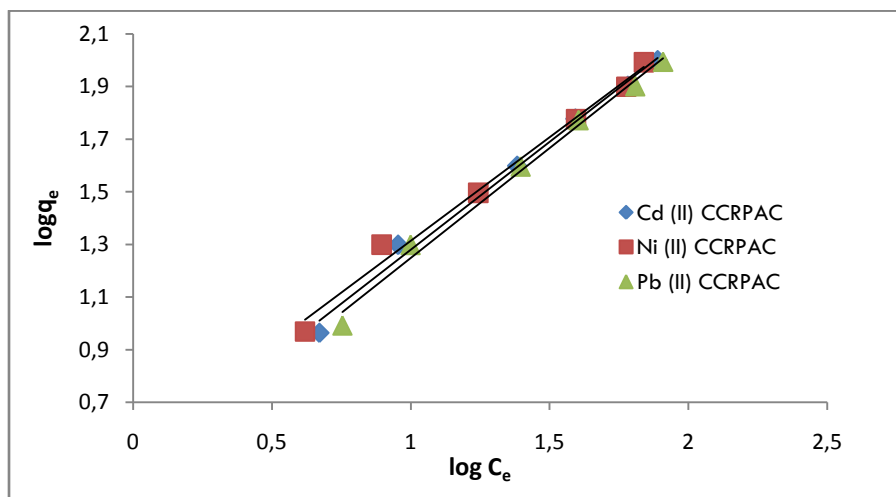


Fig 7. Freundlich isotherm model plots for adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} onto CRPAC

3.8. Thermodynamic consideration

The effect of temperature on the amount of Pb^{2+} , Cd^{2+} and Ni^{2+} adsorbed by CAC and CRPAC was further studied using the Arrhenius equation, which can be written as follows,

$$\log k = \log A - \frac{E_a}{2.303RT} \quad (8)$$

where k is the rate constant for the adsorption process, A is the pre-exponential factor, E_a is the activation energy for the adsorption process, R is the gas constant and T is the temperature. From equation 8, a plot of $\log k$ versus $1/T$ should be linear with slope equal to $E_a/2.303R$ and intercept equal to $\log A$. Figure 8 shows the Arrhenius plots for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by CAC and CRPAC. Parameters deduced from the plots are presented in Table 6. From the results presented, it can be seen that the R^2 values were close to unity indicating an excellent degree of fitness of the adsorption data to the Arrhenius model.

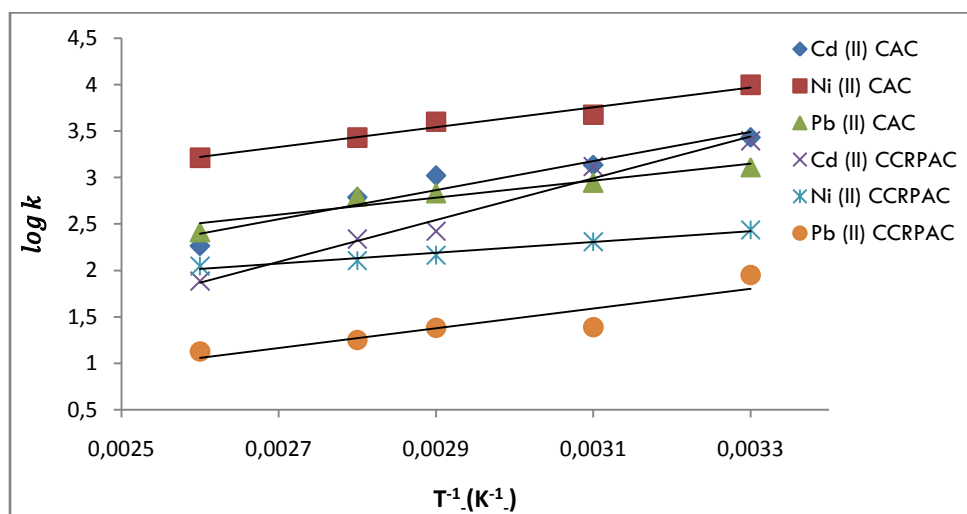


Fig 8. Variation of $\log k$ with $1/T$ for the adsorption of Pb, Ni and Cd ions by CAC and CRPAC

Table 6. Transition state parameters for the adsorption of Cd, Pb and Ni ions by CAC and CRPAC

Adsorbent	Metal Ions	slope	logA	$E_a(J/mol)$	A	R^2
CAC	Cd^{2+}	1.2825	-0.1364	24.56	0.7304	0.9300
	Ni^{2+}	1.8992	-2.2754	36.36	0.0053	0.9689
	Pb^{2+}	0.9477	-0.3679	18.15	0.4286	0.9088
CCRPAC	Cd^{2+}	1.4884	-2.3444	28.50	0.0045	0.9780
	Ni^{2+}	0.9495	-0.4690	18.18	0.3396	0.9756
	Pb^{2+}	1.6787	-3.6424	32.14	2.2782	0.8302

The thermodynamic equilibrium constants such as the standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) were estimated using the transition state equation [36].

$$\log \frac{k}{T} = \log \frac{R}{Nh} + \frac{\Delta S_{ads}^0}{2.303R} - \frac{\Delta H_{ads}^0}{2.303RT} \quad (9)$$

where k is the adsorption rate constant, T is the temperature, R is the gas constant, N is the Avogadro's number, h is the plank constant, ΔS_{ads}^0 and ΔH_{ads}^0 are the standard entropy and enthalpy changes for the

adsorption process. The mathematical implication of equation 9 is that ΔS_{ads}^0 and ΔH_{ads}^0 can be obtained from the intercept and slope of the linear plot of $(\log \frac{k}{T})$ versus $1/T$. Figure 9 shows the transition state plots for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} onto CAC and CRPAC. R^2 , ΔS_{ads}^0 and ΔH_{ads}^0 values deduced from the plots are presented in Table 7. Excellent correlations were obtained for the plots and values of ΔS_{ads}^0 were negative, which implies that there is an increasing degree of orderliness in the adsorption of the studied heavy metals ions onto the adsorbent. Also, positive values obtained for ΔH_{ads}^0 indicated that the adsorption process is endothermic.

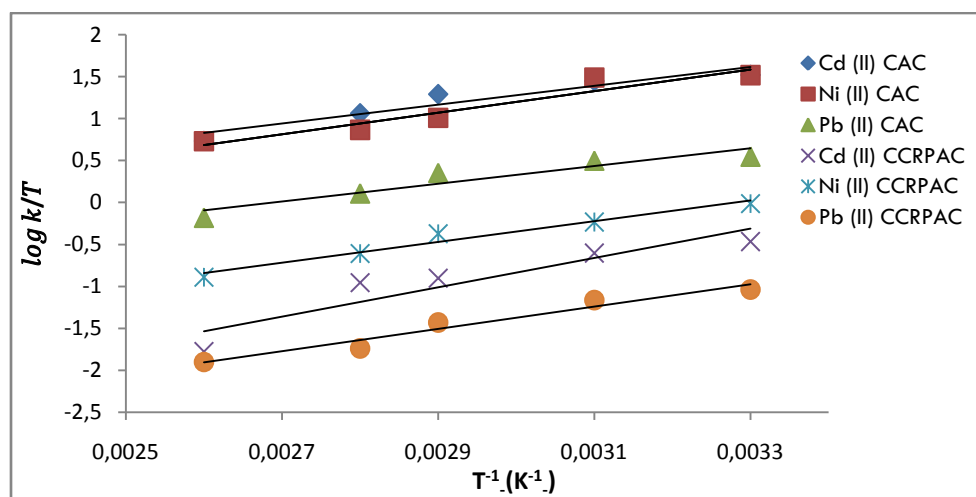


Fig 9. Variation of $\log (K/T)$ with $1/T$ for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} on to CAC and CRPAC.

Table 7. Thermodynamics parameters for the adsorption of Cd, Pb and Ni ions by CAC and CRPAC

Adsorbent	Metal Ions	Slope	Intercept	ΔH^0 (J/mol)	ΔS^0 (J/mol)	R^2
CAC	Cd^{2+}	2.4194	-5.8143	46.32	-422.14	0.7949
	Ni^{2+}	2.03134	-5.1432	38.89	-419.95	0.9192
	Pb^{2+}	0.9495	-2.6212	18.18	-364.64	0.8923
CCRPAC	Cd^{2+}	1.6633	-5.1454	31.85	-434.44	0.8560
	Ni^{2+}	1.1016	-3.4544	21.09	-386.43	0.9700
	Pb^{2+}	1.8805	-7.2141	36.01	-464.43	0.9521

4 Conclusions

The following results can be drawn from this study:

- Chitosan/raphia palm composite (CRPC) is an effective adsorbent for Cd^{2+} , Ni^{2+} and Pb^{2+} . It functions through surface adsorption.
- The modification of the chitosan by coating with raphia palm tends to increase the capacity of the chitosan as an adsorbent
- Within a certain range of the various response parameters, the adsorption of the studied heavy metals depends on the variation of concentration, biomass dose, pH and contact time.

- Thermodynamic principles can adequately be used to predict the direction of the adsorption process

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